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Simple Donor-Acceptor Molecule with Long Exciton Diffusion Length for Organic Photovoltaics

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Abstract

To succeed in commercial applications, donor materials for organic solar cells should combine high stability and simple synthesis with high performance in devices. Here, we present a new small π -conjugated molecule, TPA-T-DCV-Ph, which meets those requirements. Simple and efficient three-step synthesis produces a push-pull molecule with triphenylamine donor and phenyldicyanovinyl acceptor groups, which is suitable for both solution processing and vacuum deposition. The unique property of TPA-T-DCV-Ph is an unusually long exciton diffusion length of >25 nm due to the combined

effect of long exciton lifetime and surprisingly low energy disorder. This, together with a device engineering, resulted in >5% efficiency for TPA-T-DCV-Ph:C₇₀ vacuum-processed solar cells. The results obtained are envisioned to be further improved by optimizing the absorption of the molecule and light management in the device which can push the efficiency even further.

1. Introduction

Organic solar cells (OSCs) based on push-pull small molecules (SMs) complement advantages of polymer-based OSCs and well-established benefits of small molecules like excellent batch-to-batch reproducibility and vacuum processability [1-9]. The efficiency of SM-based OSCs keeps on increasing over the years, with record values over 10% in single-junction [10, 11] and over 13% in multi-junction vacuum-deposited [12] devices. Achieving the highest efficiencies often requires complicated multistep synthesis [10, 11] in combination with laborious device optimization [3, 5, 13-15] which essentially limits the boundaries for large-scale production of SM-based OSCs [16, 17].

Simple synthetic procedure is one of the key requirements for the organic materials to become successful in industrial mass production [16, 17]. However, SMs which show the best performance in OSCs are typically hard to synthesize (8-14 synthetic steps), which lowers the overall yield to 3-15% [11, 16-19]. The approach to simplifying the synthetic process was thoroughly explored by Roncali and coworkers [9, 16, 20-28] who designed a number of easy-to-synthesize SMs based on triphenylamine (TPA) as donor and dicyanovinyl (DCV) as acceptor blocks. Unfortunately, the efficiencies of OSCs based on easy-to-synthesize molecules typically are in the range of 3-4%, even after rigorous optimization [9, 21-23].

Next to simplifying the synthetic procedure, the major challenge lies in the optimization of the active layer [29, 30]. To maximize the quantum efficiency, one needs to match the exciton diffusion length in the active materials with the characteristic

spatial scale of donor-acceptor separation [31-34]. In typical organic materials, the exciton diffusion length does not exceed 10 nm [35-37] which enforces application of the bulk heterojunction (BHJ) concept [38]. The laborious optimization of the BHJ morphology aims at achieving a multiparameter compromise between the short exciton diffusion length, non-geminate recombination of charges and charge transport to the electrodes [39-44]. Had the exciton diffusion length been significantly larger, the very design of the OSCs would have been substantially simpler.

In this paper, we report a new molecule, TPA-T-DCV-Ph, that combines simple and efficient synthesis with long exciton diffusion length. Due to its push-pull nature, TPA-T-DCV-Ph exhibits strong absorption in the blue to red region, while a simple chemical structure and low molecular weight make it suitable for vacuum deposition. TPA-T-DCV-Ph demonstrates extremely long exciton diffusion length exceeding 25 nm in vacuum-deposited films, which is highly beneficial for simplified device optimization. Vacuum-deposited TPA-T-DCV-Ph:C₇₀ 1:1 OSCs demonstrate up to 5.1% efficiency. All these suggest high potential of TPA-T-DCV-Ph for easy-to-make mass-scale manufactured OSCs.

2. Experimental

2.1 Materials and synthesis

[1,1'-*Bis*(diphenylphosphino)ferrocene]dichloropalladium(II) Pd(dppf)Cl₂, (4-bromophenyl)diphenylamine, 2-bromothiophene, *n*-butyl lithium (2.5 M solution in hexane), magnesium, benzoyl chloride, malononitrile were obtained from Sigma-Aldrich Co. and used without any further purification. Pyridine, THF, dichloromethane and hexane were dried, purified according to the known techniques and then used as the solvents. All reactions, unless stated otherwise, were carried out under an inert atmosphere. Details of the synthesis and characterization are available in Supplementary Information (SI).

2.2 Sample preparation

Prior to deposition the substrates were cleaned with 1:10 RBS 25 concentrate (Chemical products R. Borghgraef S.A.): Di-ionized (DI) water, then rinsed with tap water and DI water and dried with N₂. 10 min exposure to O₂ plasma using a Plasma Cleaner (Harrick Plasma) helps to improve the adhesion of the first barrier layer on the anodic substrate. The layers composing the photovoltaic stack were deposited by thermal sublimation (see below for technical specifications).

The photovoltaic devices consisted of a ITO/glass substrate on which a 25 nm-thick MoO₃ barrier layer, a 100 nm-thick 1:1 (wt%) TPA-T-DCV-Ph:C₇₀ photoactive layer, 10 nm of BCP (bathocuproine as exciton-blocking layer) and a 100 nm-thick Al cathode were successively deposited. When necessary, a post-fabrication annealing treatment of the devices was performed in a N₂-filled glovebox (O₂ and H₂O within few ppm) on a Stuart SD 300 (600 W) hot plate. The ITO patterned glass substrate was purchased from Naranjo BV (thickness: ~100 nm, R_□~15 Ω.□). The materials (oxides, organic compounds, metals) were deposited by thermal sublimation in high vacuum (< 5·10⁻⁶ mBar) within a K.J. Lesker Spectros evaporating chamber. Al, MoO₃ and BCP were purchased from Sigma Aldrich and C₇₀ from Lumtec (>99% grade). No additional purification was carried out. For each sample, three devices were obtained with a 0.18, 0.20 and 0.45 cm² photoactive area, respectively; no apparent influence of the device area on the device performance was observed.

The stack architecture for the determination of the carrier mobility consisted of a 10 nm-thick layer of MoO₃ deposited on ITO, onto which a 150 nm-thick layer of TPA-T-DCV-Ph was deposited, then covered with a 10 nm-thick Yb layer to improve the charge collection [45, 46] and 100 nm-thick Al cathode. Likewise, all layers were thermally sublimated.

The stacks for PL measurements consist of a glass substrate on which layers of TPA-T-DCV (thickness: 6, 12, 24, 48 and 96 nm) are sandwiched between two 10 nm layers of C₆₀. The stacks were also thermally sublimated.

2.3 Optical

Absorption spectra were recorded with a Perkin Elmer Lambda-35 (ODCB solution) or Lambda-900 (films) spectrometers. Time-resolved PL was measured with a Hamamatsu C5680 streak-camera. The excitation (550 nm) was generated in a Newport SHG-800 hollow fiber pumped by a Mira Ti:sapphire laser.

2.4 Efficiency and mobility measurements

The photovoltaic performances of the devices were determined in the glovebox from J - V profiles obtained with a Keithley 2400 source meter. The devices were exposed to AM 1.5 irradiation provided by a Sun 2000 solar simulator (ABET Tech.). 1 sun (100 mW cm^{-2}) irradiation was calibrated using a reference Si solar cell (Rera System).

The carrier mobility was also determined from J - V profiles. At high forward bias, space charge-limited current is shown to govern charge transport in the active layer. Quadratic variation of the current with the applied bias is observed and the analytical expression of the Mott-Gurney law (See SI) in the infinite plate approximation can be used to determine the carrier mobility in the material [47].

2.5 External quantum efficiency measurements

External quantum efficiency was measured under short-circuit conditions; the device area of 0.245 cm^2 was selected by a shadow mask. The monochromatic light was produced by selecting 10 nm portions of white light (produced by an Osram 64655 HLX halogen lamp) at the given wavelengths by a set of band pass filters. The measurements were calibrated using a Si photodiode.

3. Results and discussion

Fig. 1 shows the synthetic route towards TPA-T-DCV-Ph (see SI for the detailed synthetic procedures). Synthesis of TPA-T-DCV-Ph consists of three steps (**Fig. 1**): First, diphenyl[4-(2-thienyl)phenyl]amine (**1**) was prepared in 77% isolated yield from

commercial available (4-bromophenyl)diphenylamine and 5-bromothiophene via Kumada cross-coupling using freshly prepared Grignard reagent of the latter. Second, {5-[4-(diphenylamino)phenyl]-2-thienyl}(phenyl) (**2**) was prepared by reaction of the lithium derivative of **1** and benzoyl chloride in 70 % isolated yield. Finally, TPA-T-DCV-Ph, was obtained in an 81% isolated yield by Knövenagel condensation between ketone (**2**) and malononitrile in pyridine using a microwave heating.

Simplicity and the high overall yield (44%) make the synthesis on TPA-T-DCV-Ph one of the most efficient among the known push-pull molecules developed for organic photovoltaics. The compound demonstrates good solubility in tetrahydrofuran, chloroform, and 1,2-dichlorobenzene (ODCB); the measured solubility of TPA-T-DCV-Ph in ODCB was found to be 25 g/L. The molecule demonstrates high thermal stability both in air and under nitrogen (see SI for detailed thermal properties) with decomposition temperatures at 390 °C and 400 °C, respectively, which is 100 °C higher as compared to the full analog without phenyl substituent at the DCV group [23]. The increase of thermal stability by modification of the DCV block using aromatic blocks have already been demonstrated [48-50]. This makes TPA-T-DCV-Ph a perfect candidate for manufacturing both solution and vacuum processed OSC devices.

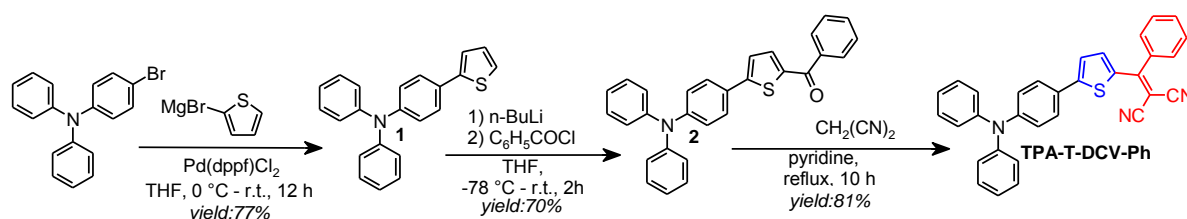


Fig. 1 Synthesis of TPA-T-DCV-Ph.

Absorption spectra of TPA-T-DCV-Ph in ODCB and in vacuum-deposited thin film are shown in **Fig. 2**. As typical for push-pull molecules, the absorption spectra consist of two bands. Usually, the high-energy band is attributed to the π - π^* transition of the conjugated backbone, whereas the lower energy absorption band is ascribed to an intramolecular charge transfer (CT) transition [25]; in reality both absorption bands

have a mixed π - π^* /CT character according to our recent studies [51].

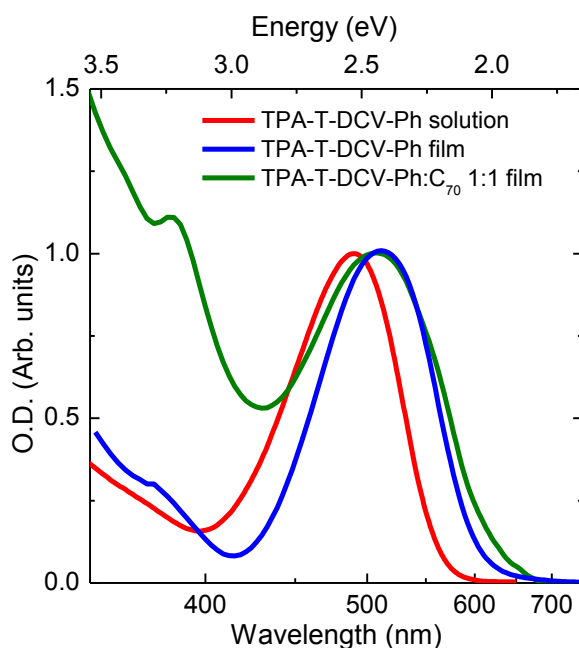


Fig. 2 UV-vis absorption spectra of TPA-T-DCV-Ph in ODCB solution (red), vacuum-deposited film (blue), and vacuum-(co)deposited 1:1 TPA-T-DCV-Ph:C₇₀ film (green).

In diluted ODCB solution, absorption peaks at 490 nm while in the vacuum-deposited film, the absorption peak shifts to 515 nm with a long shoulder extended towards ~700 nm. Absorption in the near-UV to blue region is considerably lower compared to the main peak, which makes TPA-T-DCV-Ph a perfect complementary material for C₇₀-based acceptors which absorb mainly below 500 nm.

The energies of the frontier molecular orbitals were determined by using cyclic voltammetry (CV, see SI for details). The energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are found to be -5.40 eV and -3.40 eV, respectively. Therefore, the electrochemical bandgap amounts to ~2 eV which is in good agreement with the optical bandgap obtained from absorption spectrum in thin films. The optical and electrochemical properties of TPA-T-DCV-Ph are summarized in

Table 1.

Table 1 Optical and electrochemical properties of TPA-T-DCV-Ph.

UV-vis absorption			CV		
λ_{\max}^a (nm)	λ_{\max}^b (nm)	λ_{edge}^c (nm) / E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	E_g^{EC} (eV)
490	512	605/2.05	-5.40	-3.38	2.02

^ain ODCB solution. ^bin vacuum-deposited film. ^cdetermined as the intersection between the tangent to the absorption edge in the thin film and the abscissa axis, whereas the optical bandgap is estimated as $E_g^{\text{opt}} = 1240/\lambda_{\text{edge}}$

The exciton lifetime in the vacuum-deposited TPA-T-DCV-Ph film amounts to ~1.6 ns as measured by time-resolved photoluminescence (PL) (**Fig. 3a**, 96 nm neat curve). This value is unexpectedly long for a solid film of push-pull material (where the typical lifetimes are less than 1 ns) [37, 52-55] and suggests the potential for long exciton diffusion in the vacuum-deposited TPA-T-DCV-Ph.

To confirm this hypothesis, we measured the exciton diffusion length in TPA-T-DCV-Ph by conventional interface PL quenching method [36, 37]. Briefly, the layers of TPA-T-DCV-Ph with different thicknesses (from 6 to 96 nm) were sandwiched between two 10 nm layers of C₆₀ that act as an optically neutral exciton quencher (**Fig. 3a**, see SI for details). The particular choice of the acceptor used for PL quenching measurements (e.g. C₆₀ vs C₇₀) does not influence the obtained values of diffusion lengths in TPA-R-DCV-Ph as long as the exciton quenching efficiency remains high. However, C₆₀ acceptor has a convenient advantage over C₇₀ for the diffusion length measurements because its absorption at the excitation wavelength of 550 nm is negligibly low which excludes direct acceptor excitation and therefore simplifies the data analysis.

From the exciton quenching efficiency curve (**Fig. 3b**), the three-dimensional L_d is estimated [56, 57] as ~26 nm, which is surprisingly high as compared to less than 10 nm typical for organic materials [33, 37, 58-60] (some exceptional cases like highly ordered fullerenes [56] or molecular crystals [61, 62] where the singlet exciton diffusion length may reach tens of nm notwithstanding).

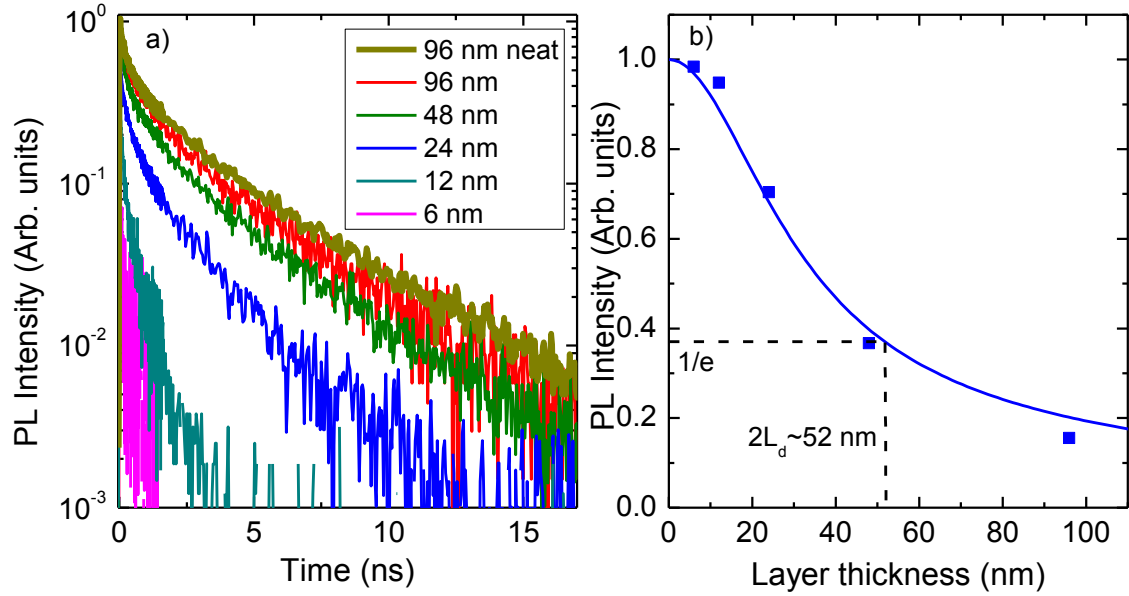


Fig. 3 (a) PL transients upon 550 nm excitation for the TPA-T-DCV-Ph trilayer samples. All transients are integrated in the 580-850 nm spectral range and normalized by the sample absorption. (b) PL quenching efficiency vs. TPA-T-DCV-Ph layer thickness. The experimental values are shown by symbols while the solid line is the best fit with Eq. (3), SI. Doubled value of L_d is determined as the distance of $1/e$ exciton harvesting efficiency.

Generally, the exciton diffusion length depends on the exciton diffusion coefficient D and the exciton lifetime T_1 as $L_d \sim \sqrt{DT_1}$ [37]. The exciton diffusion coefficient strongly depends on the energetic disorder of the material: high disorder results in formation of low-energy sites that act as traps and slow down exciton diffusion [31, 37, 63]. Typically, in organic materials the disorder is fairly high ($\sigma > 70$ meV) which significantly limits D [64-67]. We extracted the energetic disorder for TPA-T-DCV-Ph vacuum-evaporated film as $\sigma \sim 45$ meV from the transient shift of PL maximum (see SI, Figure S12). Therefore, the high value of L_d in TPA-T-DCV-Ph is determined by both exceptionally long exciton lifetime and low energetic disorder.

Fig. 4 shows current-voltage characteristics of the best vacuum-deposited OSC based on TPA-T-DCV-Ph as a donor and C₇₀ as an acceptor under AM1.5 illumination

(see Figure S14 in SI for the statistics over 18 devices). The active layer absorbs a significant fraction of incoming photons in near-UV to visible region (**Fig. 2**, the green line); however, the blend lacks absorption of near-IR light. External quantum efficiency (see Figure S18 in SI) follows nicely the absorption profile of the device indicating efficient charge generation from both TPA-T-DCV-Ph and C₇₀ phases.

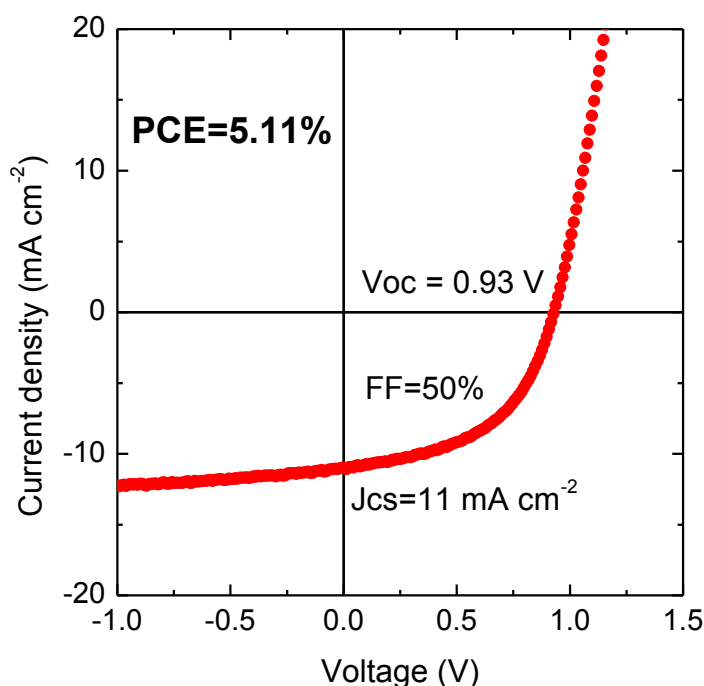


Fig. 4 Current-voltage characteristic of the best 1:1 TPA-T-DCV-Ph:C₇₀ 100 nm thick BHJ OSC; for the statistics over 18 devices refer to SI. Device area is 0.20 cm², the device parameters are indicated next to the curve.

The OSCs demonstrate high V_{OC} =0.93 V, J_{SC} =11 mA cm⁻² and FF =50%. Remarkably, the TPA-T-DCV-Ph:C₇₀ OSC features extremely low V_{OC} loss of 0.3 V (calculated as $(E_{LUMO}^{C70} - E_{HOMO}^{Donor})/e - V_{OC}$), although typical V_{OC} losses in OSCs are much higher and can exceed 1 V [68, 69]. Note that the values of HOMO and LUMO energy levels quoted in the literature (and also herein) typically do not take into account any interfacial and/or film packing effects which may significantly influence the energy level positions of the materials in BHJs. Therefore, the V_{OC} losses quoted can serve only as an estimated value.

Low V_{OC} losses were also previously found in linear [70] and star-shaped [54] TPA-DCV-based molecules. Partially, the low V_{OC} loss in TPA-T-DCV-Ph:C₇₀ is explained by the low energy disorder [71] of TPA-T-DCV-Ph; however, the share of disorder-induced V_{OC} losses to the total losses are typically only ~ 0.1 V [72]. Therefore, one can conclude that in addition to high exciton diffusion and low energy disorder, TPA-T-DCV-Ph:C₇₀ system features extremely low recombination losses [72, 73] which altogether lead to both high V_{OC} and J_{SC} . As a result, the devices show efficiency of up to 5.1% (averaged efficiency over 18 devices is $4.4 \pm 0.4\%$). These results clearly suggest outstanding performance of TPA-T-DCV-Ph as donor material for vacuum-deposited OSCs.

4. Conclusions

In summary, we have demonstrated a simple and efficient three-step synthesis of a new push-pull molecule for photovoltaic applications, TPA-T-DCV-Ph. The molecule demonstrates broad absorption in visible region complementary to absorption of C₇₀-based acceptors, and is suitable for both solution and vacuum processing. The unique advantage of TPA-T-DCV-Ph is an extremely long exciton diffusion length (~ 26 nm) in the vacuum-evaporated phase that originates from both long exciton lifetime (~ 1.6 ns) and low energy disorder (~ 45 meV). This results in simplified optimization of TPA-T-DCV-Ph-based solar cells: an OSC device based on 1:1 of TPA-T-DCV-Ph:C₇₀ mixture demonstrates over 5% efficiency. Therefore, TPA-T-DCV-Ph presents an example of easy-to-synthesize organic materials for high-performance solar cells suitable for mass-scale device production. We envision further improvement of the efficiency achieved by extending the absorption of the donor molecule to near-IR by chemical engineering and designing high-performance layered solar cells.

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